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# AN AIR POLLUTION ASSESSMENT OF HYDROGEN FLUORIDE

AIR FORCE ENVIRONMENTAL TECHNICAL APPLICATIONS
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MARCH 1976

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## USAF ENVIRONMENTAL
## TECHNICAL APPLICATIONS CENTER

SCOTT AIR FORCE BASE, ILLINOIS 62225

REPORT 7785

AN AIR POLLUTION ASSESSMENT
OF HYDROGEN FLUORIDE

By

Capt Richard W. Fisher

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March 1976

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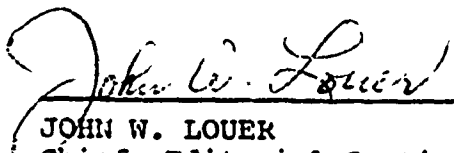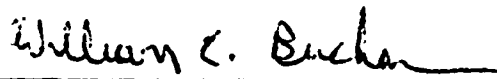
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| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|---|
| 1. REPORT NUMBER<br>USAFETAC 7785 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>An Air Pollution Assessment of Hydrogen Fluoride | | 5. TYPE OF REPORT & PERIOD COVERED |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s)<br>Richard W. Fisher, Capt, USAF | | 8. CONTRACT OR GRANT NUMBER(s) |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>US Air Force Environmental Technical<br>  Applications Center (USAFETAC)<br>Scott AFB IL 62225 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>US Air Force Environmental Technical<br>  Applications Center (USAFETAC)<br>Scott AFB IL 62225 | | 12. REPORT DATE<br>March 1976 |
| | | 13. NUMBER OF PAGES<br>30 |
| 14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office) | | 15. SECURITY CLASS. (of this report)<br>Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Air Pollution                 Gaseous Diffusion
Dispersion Models             Mesoscale Diffusion
Hydrogen Fluroide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Only generalized conclusions about ground level concentrations ($\chi$) of hydrogen fluoride (HF) are possible when the place and time of aerial release are unknown. HF is assumed to be a gas when released from altitudes of 3 km and 10 km and remains a gas during the entire diffusion process. Three line-source models are solved for $\chi/Q$ since the emission rate, $Q$, is unknown. H. Cramer's concentration model is the product of five terms, including an

Block 20 continued

edge effects term borrowed from Turner. Ground level dosages are also included. B. Turner's line-source model is a direct modification of Sutton's basic diffusion equations and uses vertical and horizontal standard wind deviations as calculated by Cramer. The third model is an empirical derivation from Air Force testing at the Cedar Hill Tower, Dallas, Texas. Results from these three models graphically depict the maximum ground concentrations of HF at 60 km downwind. Theoretically, when HF is released at 10 km altitude the maximum ground concentration occurs beyond 100 km, at which distance these equations become ineffectual. However, these estimated concentrations represent only the worst meteorological conditions. Therefore, only when the mixing depth is high will concentrated HF contamination occur.

## PREFACE

The US Air Force Environmental Technical Applications Center (USAFETAC) prepared this report in answer to a request from the Argonne National Laboratory, Argonne, Illinois. The information is provided in support of the Air Force Weapons Laboratory (AFWL) Project 19008W15, "Environmental Implications of Airborne Hydrogen Fluoride (HF) Laser Operations."

Argonne National Laboratory requested USAFETAC support in the belief that USAFETAC maintains a working computer diffusion model for gases released from elevated line sources. USAFETAC does not have a working computer model; therefore, this report presents generalized conclusions based upon a thorough search of references that present information relevant to this problem.

In the event that this report is incorporated into another report by the requester or any other agency, request that USAFETAC be furnished a copy of the new report in all cases where such dissemination is not prohibited.

USAFETAC prepared this report for a specific purpose; therefore, any further application of this information should be undertaken with caution. Work on this report progressed under rigid constraints of resources including time, personnel, equipment, and data. Department of Defense agencies and their contractors should contact USAFETAC directly for aid in assessing the applicability of this material for their purposes. Other prospective users should contact professional environmental analysts in the National Oceanic and Atmospheric Administration (NOAA) or private industry for similar assessment service.

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# AN AIR POLLUTION ASSESSMENT OF HYDROGEN FLUORIDE

## Introduction

The purpose of this report is to estimate the diffusion characteristics and downwind concentrations of hydrogen fluoride (HF) after it is released from an airplane. The author conducted an exhaustive search of USAFETAC's in-house technical library to determine a method or methods adaptable to this problem.

Several authors have modified Sutton's basic diffusion equations for microscale analyses. Applications from three sources are included in this report. The most useful model, H. H. Cramer (3), offers a generalized concentration model for a finely divided particulate or gas using the Gaussian distribution functions. The second model, applied by D. B. Turner (9), rewrites Sutton's (1932) concentration equation into a simplified finite line source model including an edge effects term (EET). This term is also applied as the EET to Cramer's Generalized Model in this report. The third model is a reapplication of an equation by Smith and Hay (1961) using vertical turbulence intensity (7). The US Air Force empirically tested the diffusion characteristics of airborne substances near Cedar Hill, Texas and then appropriately modified the original equation. Under steady-state conditions, estimates can be made using these equations for distances of up to 100 kilometers. These line-source equations are briefly described in this report. However, the classical diffusion equations are not appropriate for unsteady-state diffusion estimates (5:17,19).

1.

## Assumptions

The state of the art of diffusion estimation and the limited amount of input data require that several assumptions be made. They are:

(1) Diffusion in the alongwind or x-direction can be neglected when compared with a strong transport wind (5:13).

(2) In the vertical direction HF assumes a statistical Gaussian distribution.

(3) The emission is an instantaneous line source.

(4) Homogeneous steady-state conditions exist (i.e., no space or time changes in wind or turbulence).

(5) HF reflects perfectly at the surface (i.e., no ground absorption) and at the height of the mixing layer.

(6) HF remains a gas.

(7) No HF coalesces with water vapor, or washes or rains out.

(8) HF has approximately the same molecular weight as air (i.e., no thermal buoyancy or settling velocity).

(9) Atmospheric stability is neutral at all points downwind.

(10) Mixing height equals height of release.

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(11) The mean wind direction is normal to the airplane's flight path.

(12) No vertical wind shear at any point.

(13) The emission rate is constant.

## Data Provided

We are given or can calculate several pieces of information.

Mean Wind Speed (m) = 20 m/s (45 mph)

Sampling will take place near the surface therefore

$z = 2$ meters

Four runs will be made:

| Run | Speed of Aircraft Mach | (m/s) | Altitude of Release (H) | Length of Release (y) |
|-----|------------------------|-------|-------------------------|------------------------|
| (1) | .5 | (230) | 3 km (10,000') | 3,450 m |
| (2) | 1.5 | (760) | 3 km | 10,350 m |
| (3) | .5 | | 10 km (33,000') | 3,450 m |
| (4) | 1.5 | | 10 km | 10,350 m |

## Summary

Hydrogen fluoride (HF) is a very stable substance in the atmosphere. Anhydrous HF or partially hydrolyzed HF is completely soluable in the presence of sufficient quantities of water vapor. Thus, in order to avoid coalesence and precipitation scavaging, no water vapor is

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assumed to be present. At various temperature and
pressure conditions present in the atmosphere HF may
become a liquid, although it is conveniently assumed to
always be a gas here. Gaseous HF is slightly lighter
than air but for these computational purposes it will
have the same mass. Thus, only mechanical mixing is
considered in this report. Using the given and calculated
data and the line source dispersion equations found in
Appendix A, we can estimate ground-level and release-level
concentration/emission rate values ($\chi/Q$ in $sec/m^3$) and
dosages at pertinant distances downwind.

Table 1. Estimated Ground Level Concentrations (from
Cramer (1))

| Concentrations ($sec/m^3$) | Distances Downwind | |
| --- | --- | --- |
| | 60 km | 100 km |
| *$(\chi/Q)_3$ | $4.0 \times 10^{-5}$ (max) | $3.9 \times 10^{-5}$ |
| *$(\chi/Q)_{10}$ | $8.0 \times 10^{-7}$ | $4.0 \times 10^{-6}$ |
| Dosage$_3$ | $4.0 \times 10^{-5}$ (max) | $3.9 \times 10^{-5}$ |
| Dosage$_{10}$ | $2.8 \times 10^{-8}$ | $4.0 \times 10^{-6}$ |

*Subscripts denote release from 3 km and 10 km.

Maximum values for releases at 10 km altitude are
given for 100 km downwind. The mathematical peak occurs
beyond that distance but the model may not be accurate
past 100 km. If the mixing is below the release height

of the HF gas, virtually no ground contamination will
occur.

Consistant and accurate meteorological inputs are
paramount for the successful application of any pollution
concentration estimation method. Among the meteorological
parameters, the mixing depths downwind from the release
point are the most important factors in determining cloud
expansion and ground contamination.

The assumptions made at the outset of this report
make the expected concentrations extreme worst case figures.
This conservatism means that under virtually all meteoro-
logical conditions, the expected concentrations will not
exceed those given.

## Discussion

Using Cramer's equation (3:21) we can calculate
center line concentrations and graph the results for
$\chi/Q$ values at the release height (Figure 1) or at the
ground level when released from 3 km (Figure 2). When HF
is released from 3 km, the maximum ground level concent-
ration occurs 60 km downwind and the corresponding $\chi/Q$ is
is $3.22 \times 10^{-5}$ sec/m$^3$.

When HF gas is released from an altitude of 10 km,
the maximum concentration theoretically occurs 200 km
downwind and is about $10^{-5}$ sec/m$^3$. However, Cramer's
steady-state equation is not valid beyond 100 km. At
this distance $\chi/Q$ is about $5.2 \times 10^{-6}$ sec/m$^3$.

The EET (Figure A-4) is a function of the length
of the spray line, y, which, when considering a constant
emission time, varies directly with aircraft speed. Thus,
at Mach 0.5, the concentration values at either edge of
the 3450 meter spray line falls off by only 4% while at
Mach 1.5, virtually no concentration loss can be noticed
at the spray line's edge.

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Figures 3 and 4 give the vertical term (VT) versus the distance downwind for a release altitude of 10 km. Similar calculations for using the edge effects term can be made for the release height.

Figure 5 illustrates the estimated center line dosage term versus distance downwind. This is interpreted as the amount of HF that passes a point during an entire spray episode. The EET (Figure A-4) is applicable to the dosage terms as well.

Figures 6 and 7 show the expected ground level concentration of HF when released from an altitude of 3 km and 10 km respectively.

Other investigations to determine the actual downwind concentration from elevated line sources have been conducted using empirical experiments. Among them was an Air Force test at the Cedar Hill, Texas television tower (7:171). The Air Force released traces of zinc cadmium sulfide from a low flying aircraft while samplers were placed at regular intervals downwind to 48 km. The experimenters related cloud expansion to meteorological parameters including vertical and horizontal turbulence and wind velocity. In a well developed turbulent layer, estimated ground level concentrations agreed well with the mathematical model listed below.

$$C/Q = \frac{2}{3x\bar{u}\sqrt{2\pi}} \exp -\left[\frac{H^2}{18x^2}\right] \qquad (1)$$

"For releases above this turbulent layer, ground exposures were much more erratic than predicted by the model (1:171)."

When vertical turbulence is unity the released altitude concentration can be plotted for distances downwind (Figure 8). Cramer's VT, calculated above, can be used together with the above C/Q to estimate ground level concentrations.

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Turner (9:41) developed an equation to estimate
downwind concentrations at the ground from a finite line
source. The wind must be normal to the spray line. The
standard deviation in the vertical, $\sigma_z$, is taken from
the calculations for Cramer's model.

Figure 9 is an illustration of the estimated down-
wind ground concentrations from Turner's equation:

$$\chi/Q = \frac{2}{2\pi \, \sigma_z u} \; \exp\left[-1/2\,(-1/2\,(\frac{H}{\sigma_z})^2\right] \qquad (2)$$

For distances greater than 100 km downwind, in the meso-
scale under turbulent conditions, or in the macroscale,
the classical diffusion equations are not appropriate.
Predictions of concentration distributions are more
accurately made with synoptic forecasts of the movement
of large air masses. USAFETAC does not have the capability
to make large scale turbulence predictions at this time.
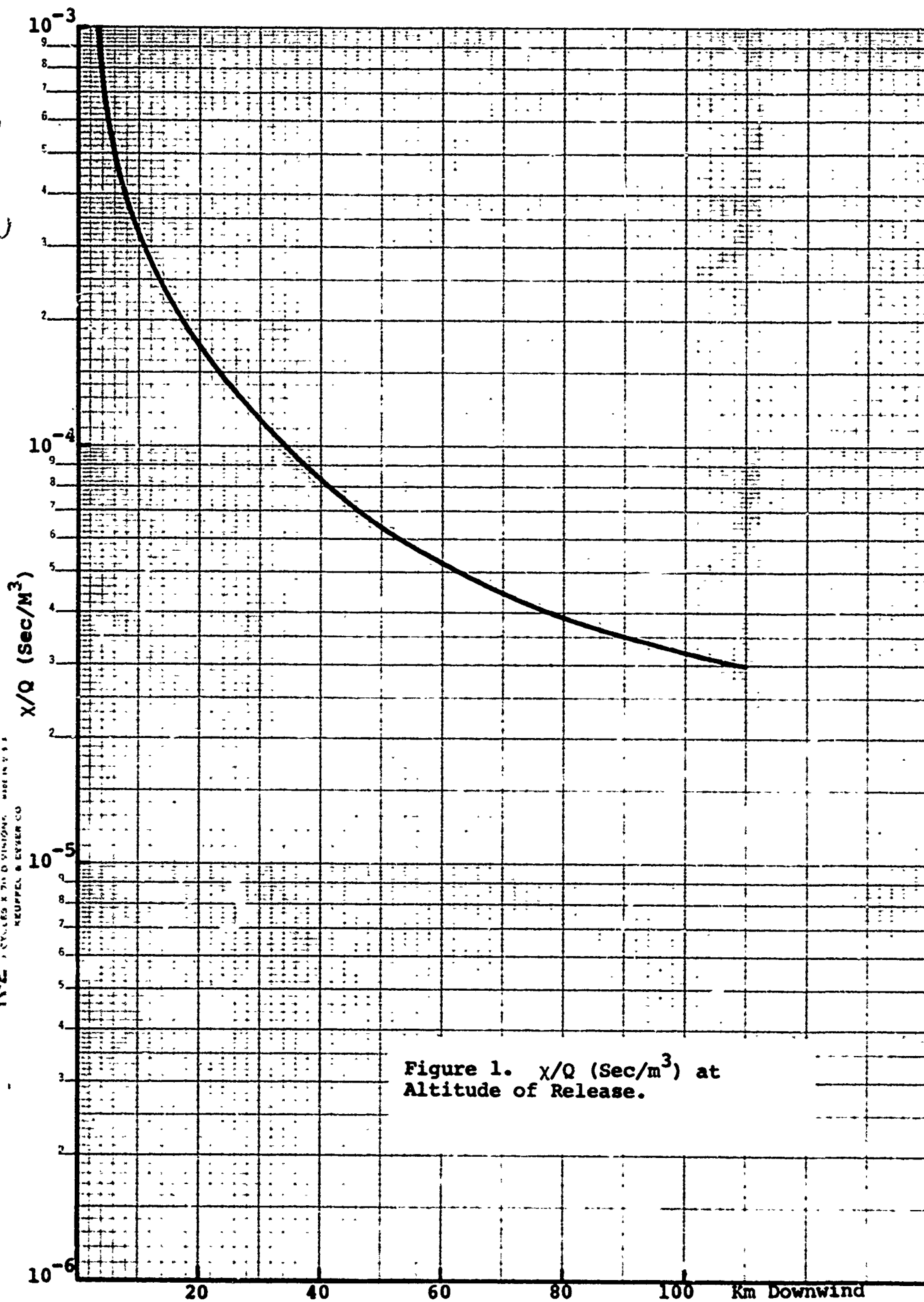
Figure 1. $\chi/Q$ (Sec/m$^3$) at Altitude of Release.
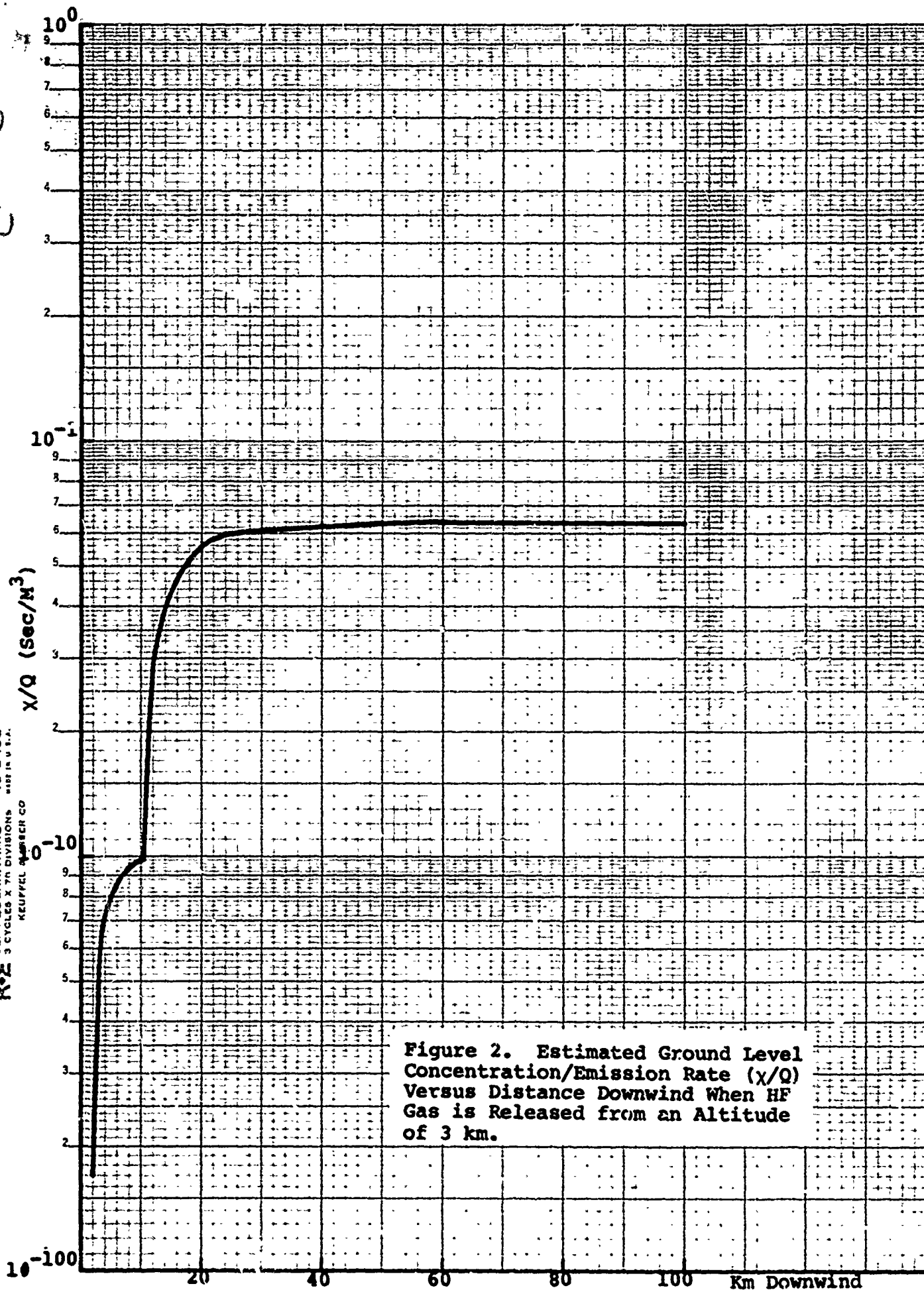
Figure 2. Estimated Ground Level Concentration/Emission Rate ($\chi/Q$) Versus Distance Downwind When HF Gas is Released from an Altitude of 3 km.

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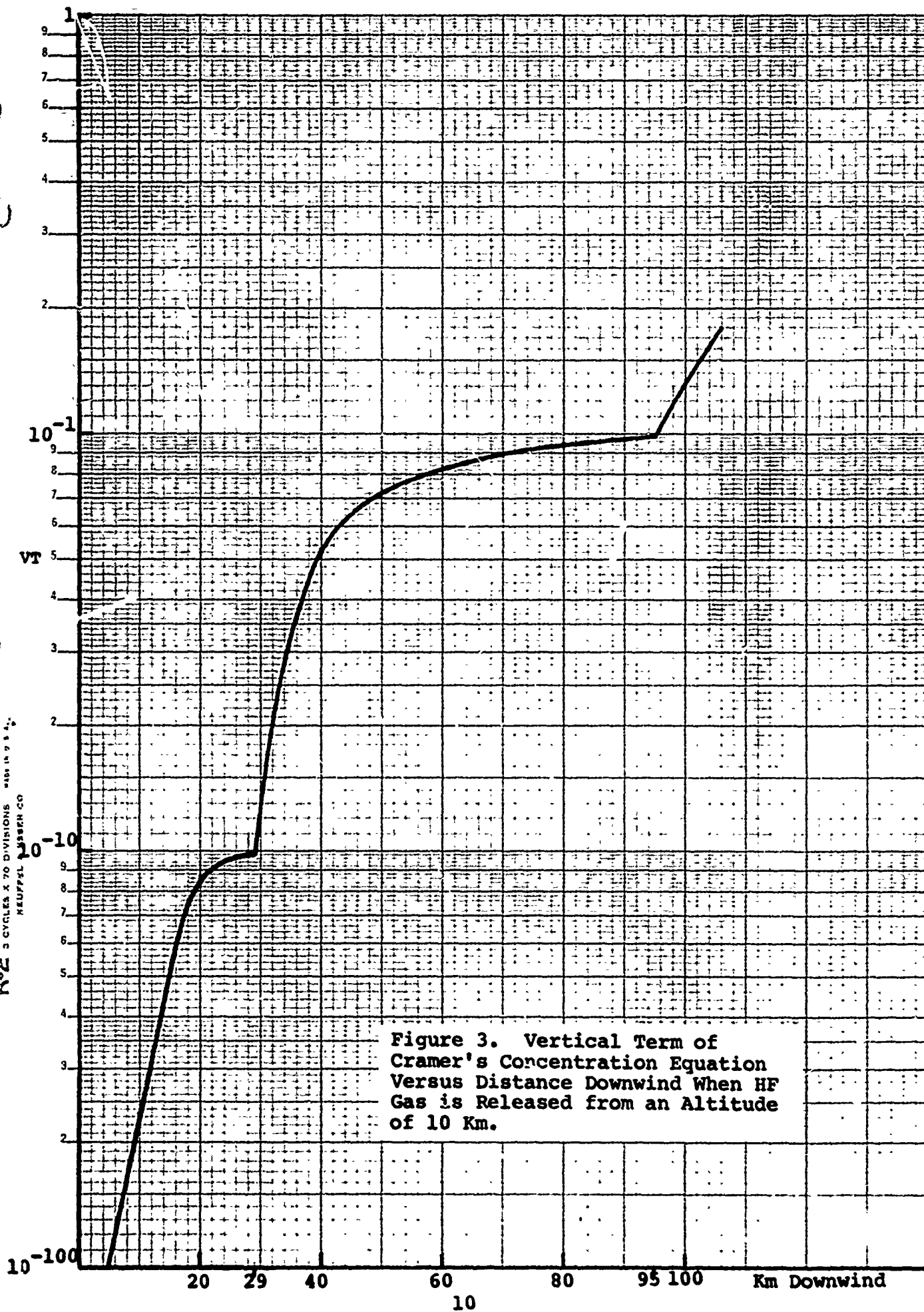
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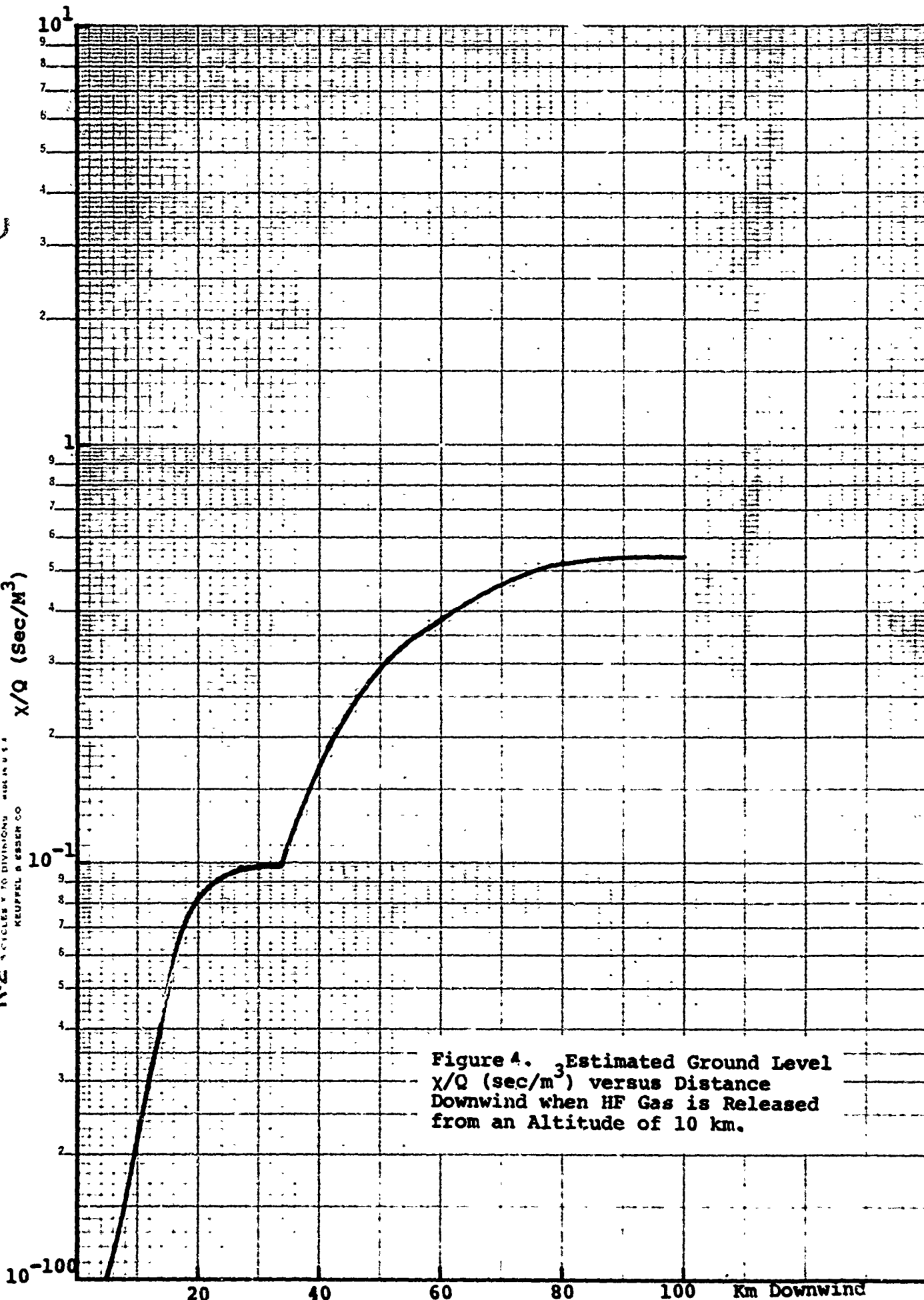
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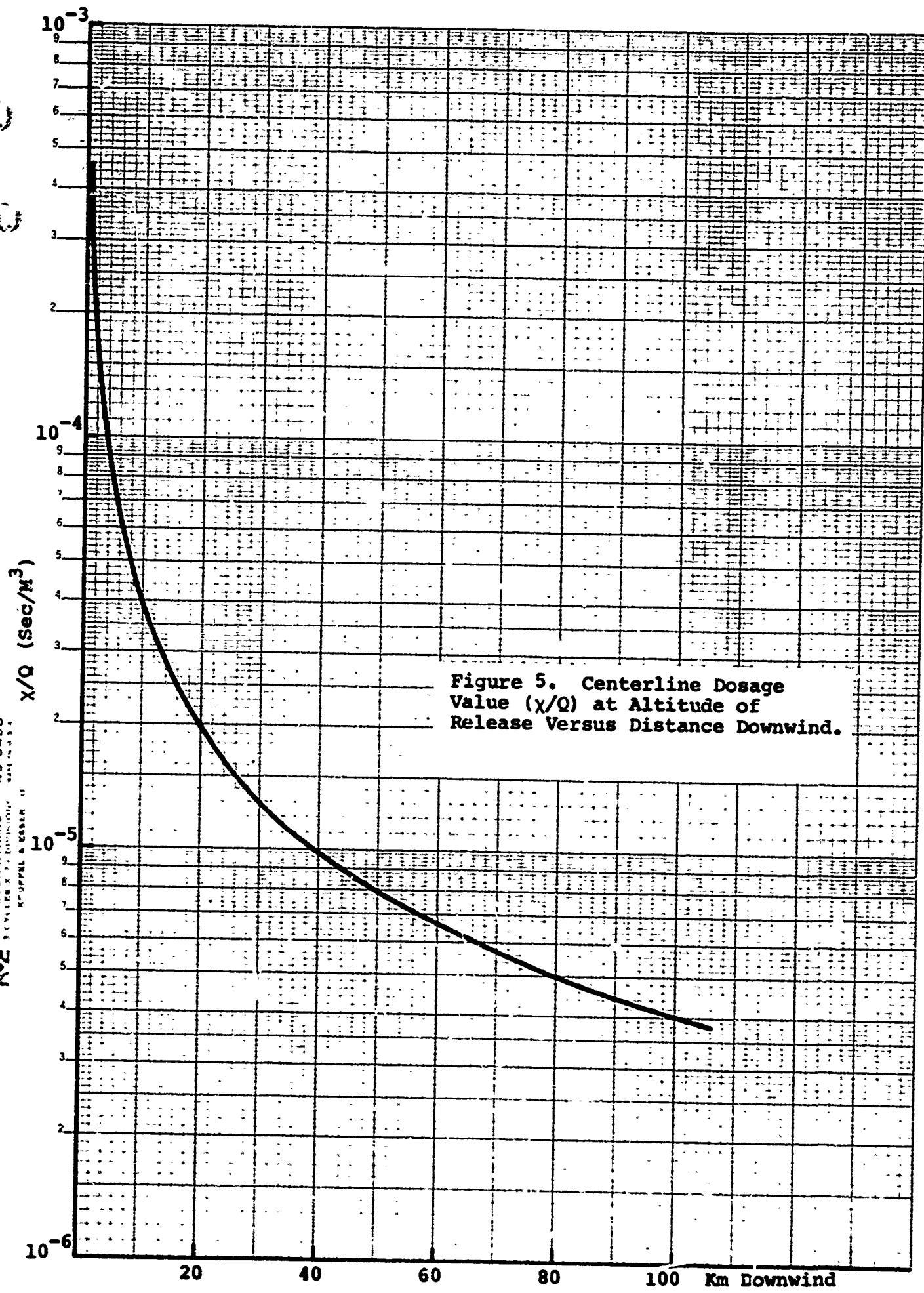
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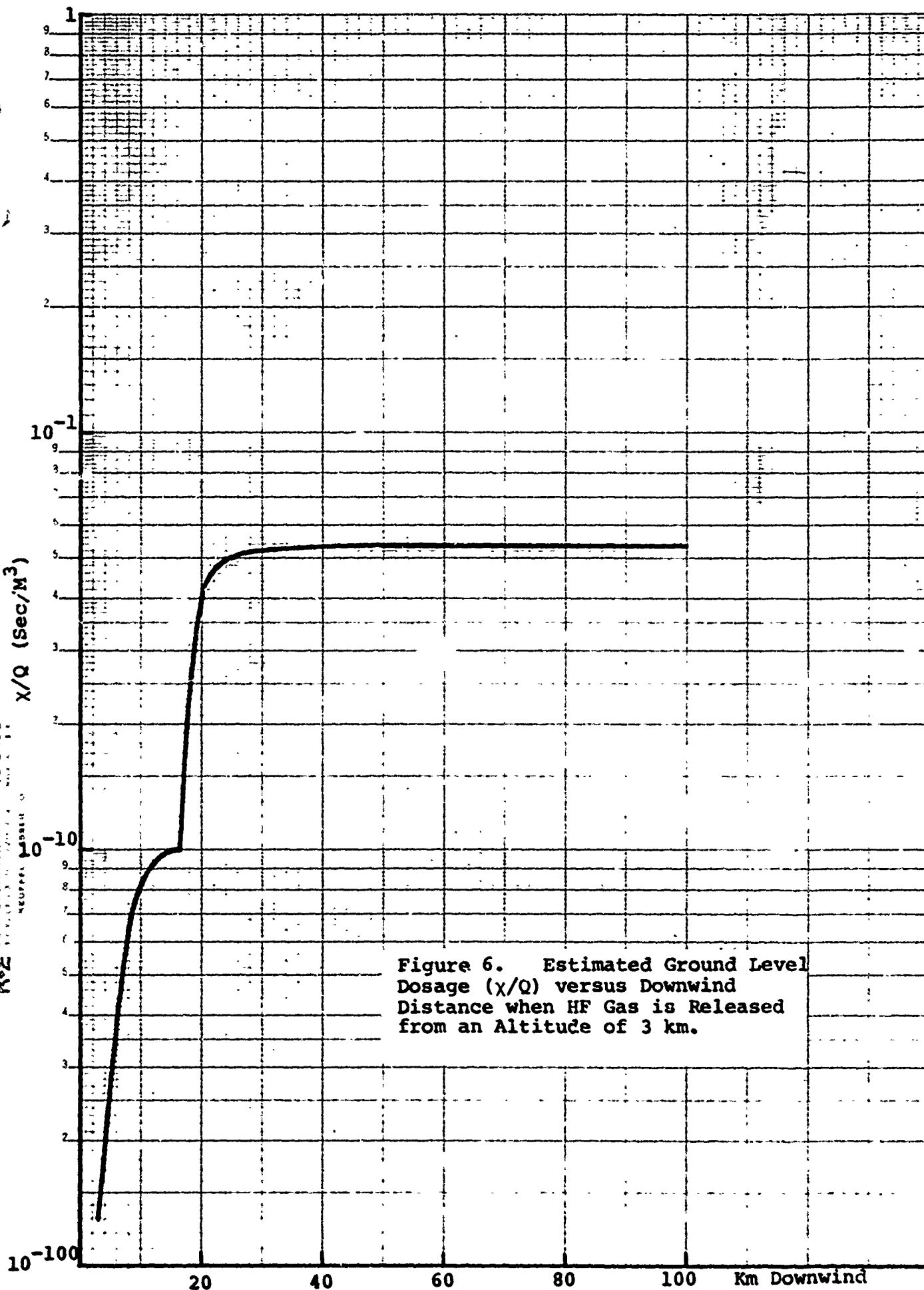
Figure 6.    Estimated Ground Level
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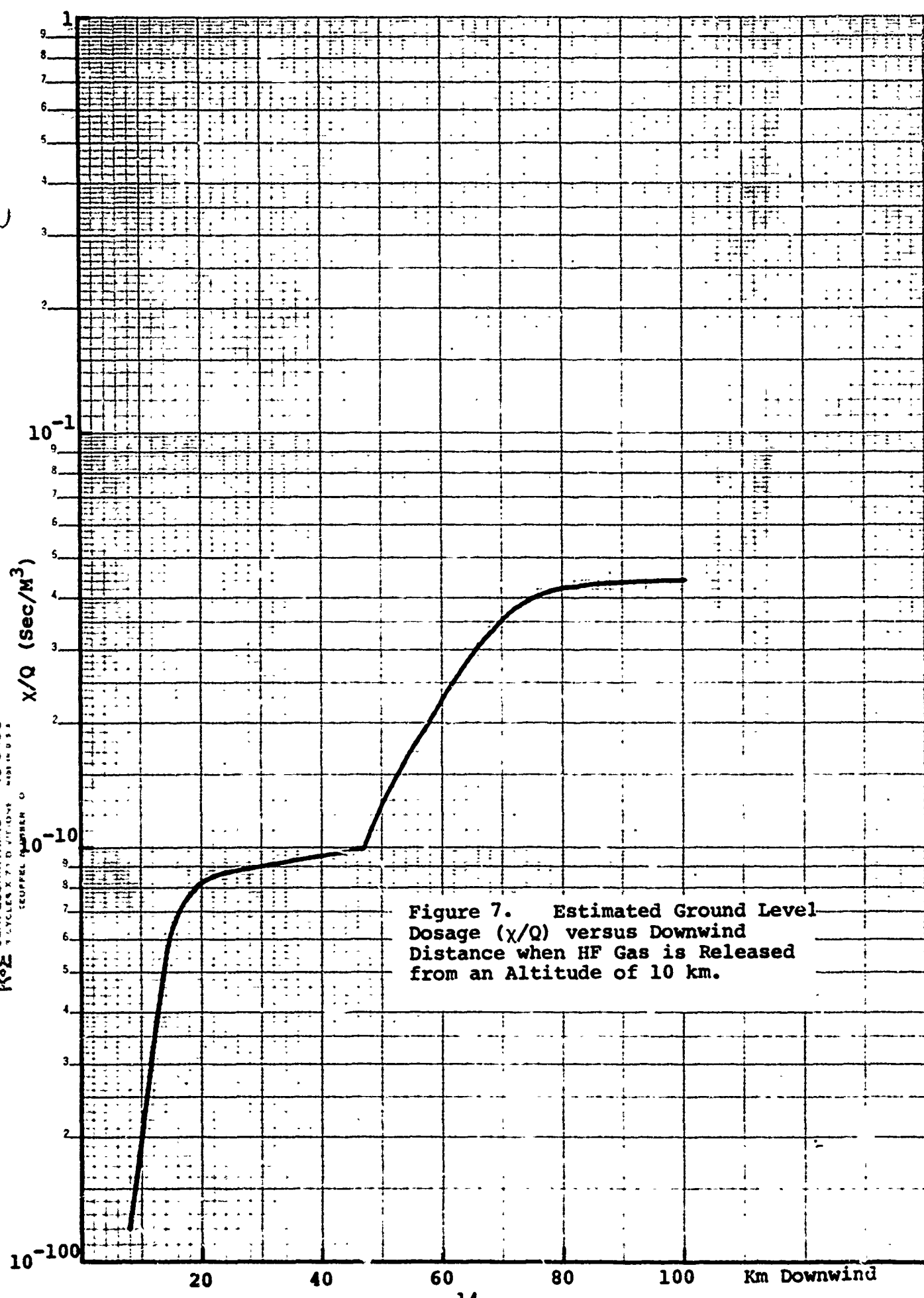from an Altitude of 3 km.

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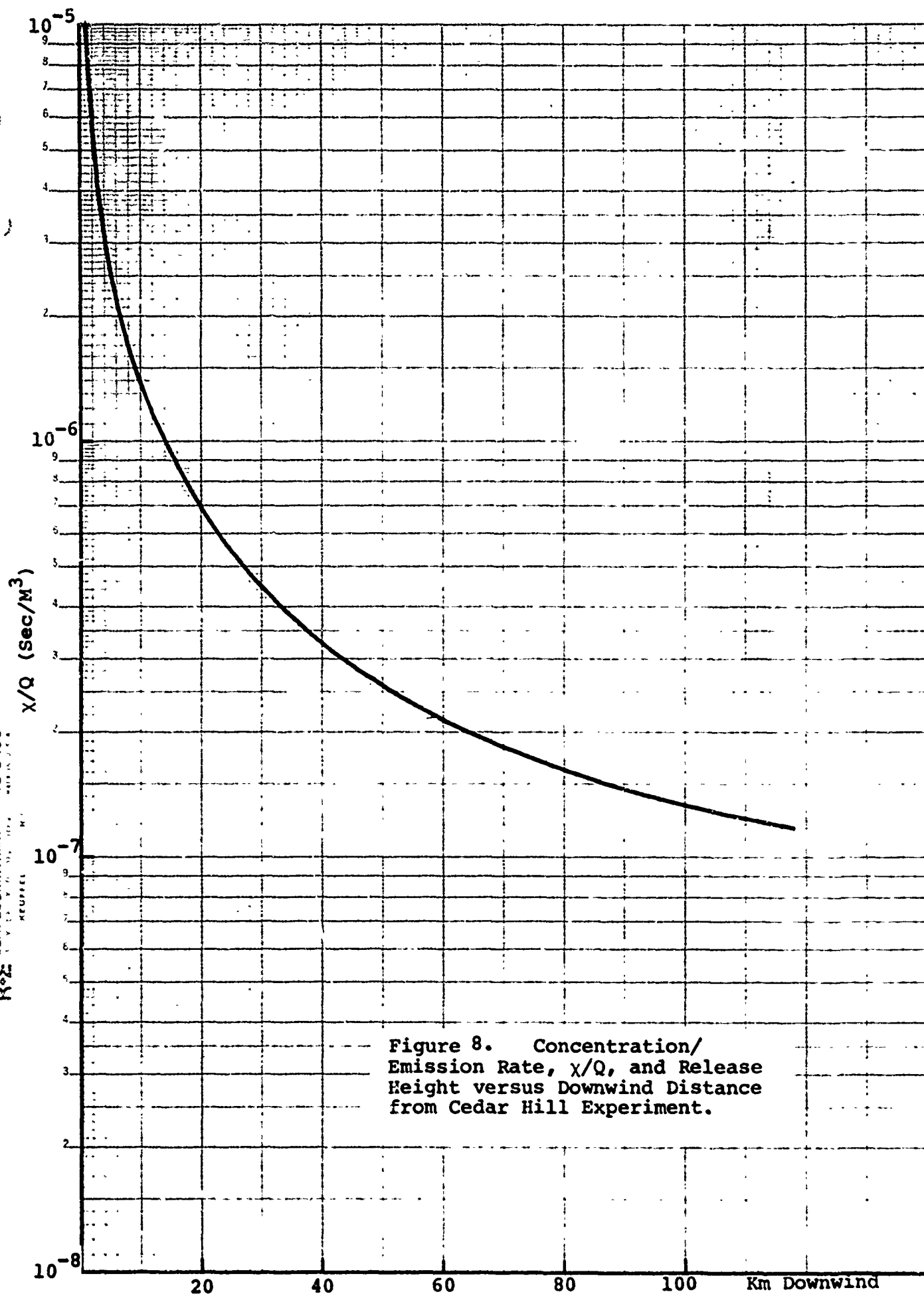
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Figure 8.  Concentration/ Emission Rate, $\chi/Q$, and Release Height versus Downwind Distance from Cedar Hill Experiment.
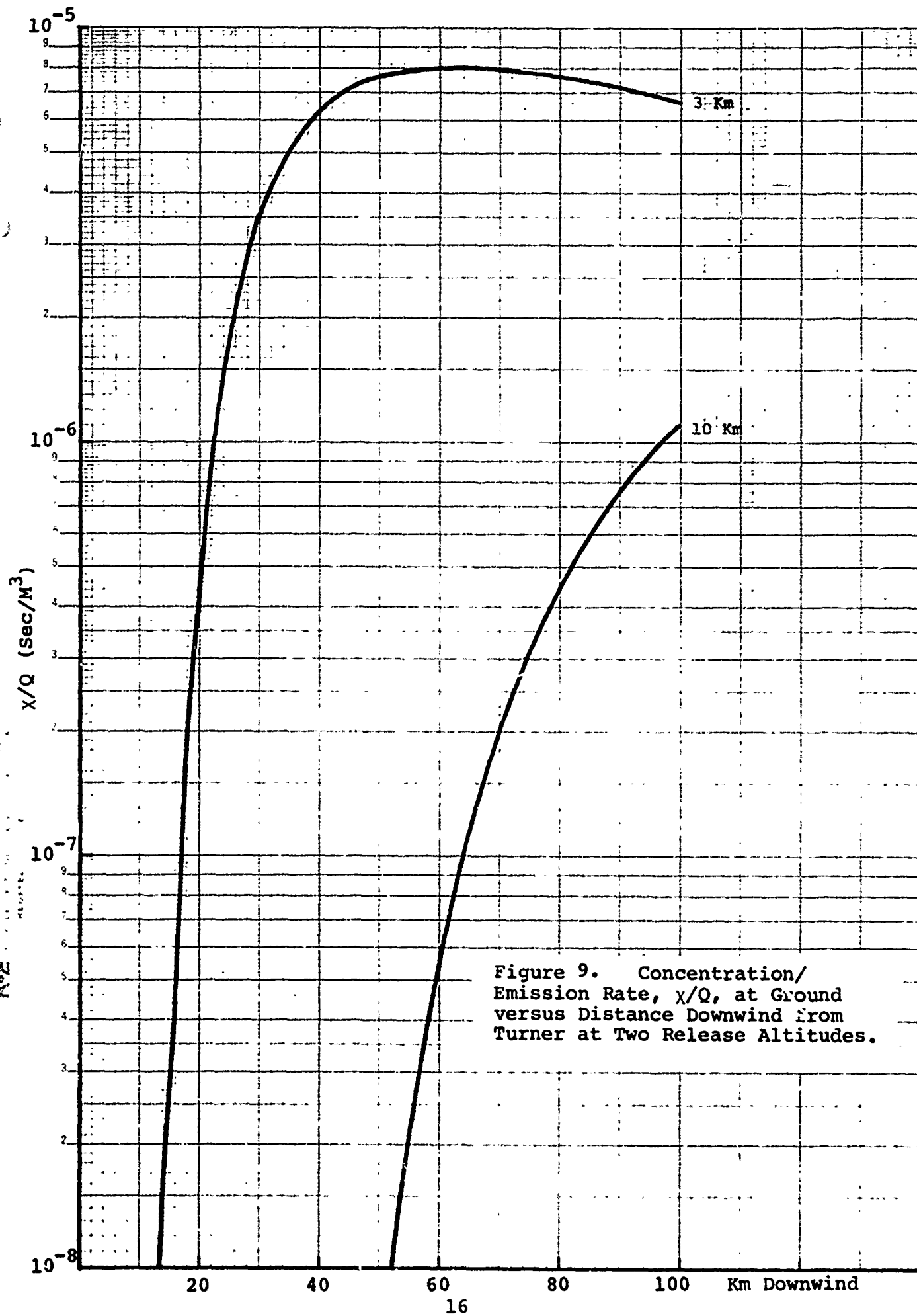
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Figure 9. Concentration/ Emission Rate, χ/Q, at Ground versus Distance Downwind from Turner at Two Release Altitudes.

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## Appendix A

## CALCULATIONS FOR CRAMER'S GENERALIZED CONCENTRATION MODEL

Cramer (3:21) uses a generalized mathematical prediction model containing five terms to calculate downwind line source concentrations. The model is simply written:

$$\text{Concentration } (\chi) = CCT \times VT \times EET \times AT \times DT \qquad (A-1)$$

where

$CCT$ = Centerline Concentration Term

$$= \frac{Q}{2\pi\sigma_z\sigma_x} \qquad (A-2)$$

The emission rate, $Q$, is unknown, therefore when we solve for $\chi/Q$,

$$CCT = \frac{1}{2\pi\sigma_z\sigma_x} \qquad (A-3)$$

where

$\sigma_z$ = standard deviation of vertical concentration distribution

$$= \sigma_E'(x_{rz}) \left[\frac{x + x_z - x_{rz}(1-\beta)}{\beta x_{rz}}\right]^\beta \qquad (A-4)$$

where

$$\sigma_E' = \sigma_A/3 \qquad (A-5)$$

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where

$$\sigma_A = \text{standard deviation of the wind}$$
azimuth (it can be interpolated
from Figure A-1)

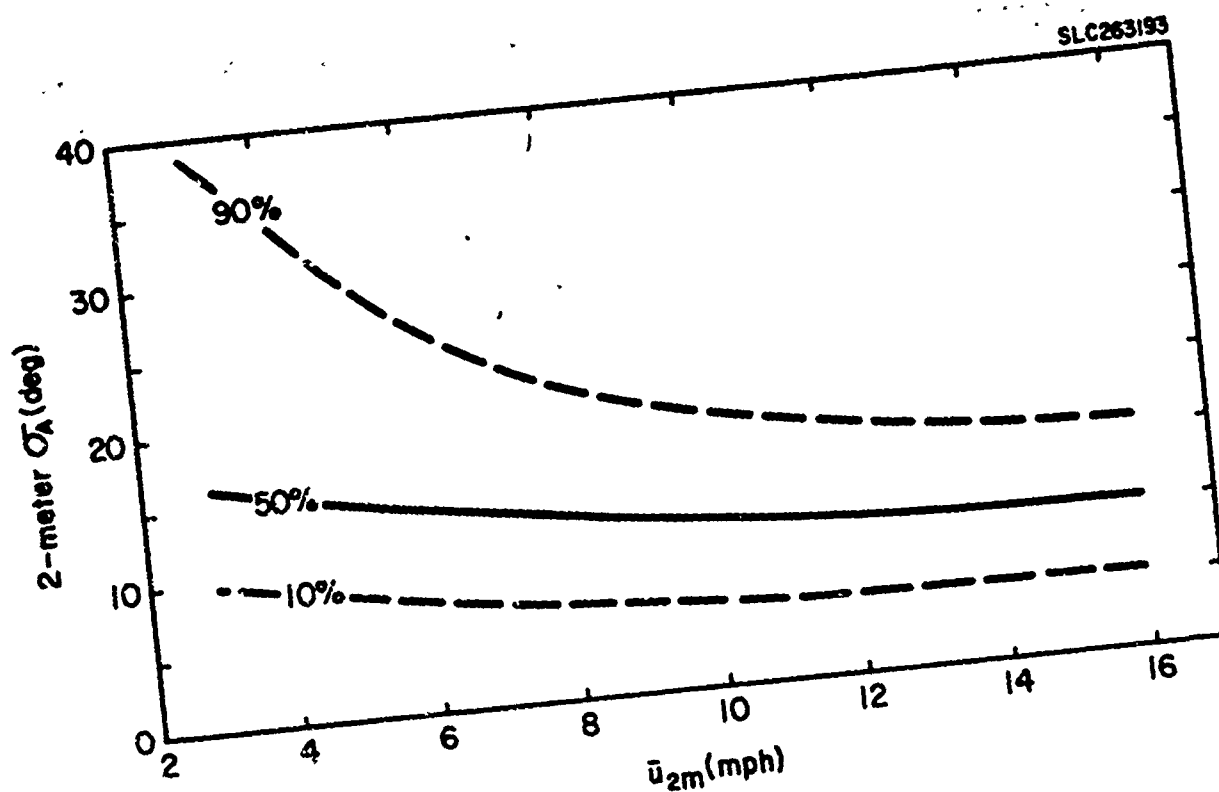$$= 10 \text{ (using the median expected value,}$$
50% at 20 m/s)



Figure A-1. Relationship Between the Wind Speed 2 Meters Above the Ground and the 10 Minute Standard Deviation of Wind Azimuth Angle ($\sigma_A$) in the Daytime (3:52).

$$x_{rz} = \text{distance downwind at which cloud}$$
stabilization occurs - experience
shows that a conservative estimate
is about 20 meters.

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$\beta$ = vertical diffusion coefficient (3:63)
references sources that show this value
approaches unity for elevated releases
under neutral conditions.

$x_z$ = vertical virtual distance - when the
standard deviation of the vertical
concentration distribution is small,
this value

$$= \frac{\sigma_{zR}}{\sigma_E^T} - x_{Rz} \qquad (A-6)$$

$$= 1/3.3 = 0.30$$

$x_{Rz}$ = distance downwind at which the
standard deviation of the vertical
concentration distribution is
measured
= $\emptyset$ (since we are interested only
in the standard deviation at the
source)

thus, as an example, assume that we are interested in a
distance 10 km ($10^4$m) downwind,

then

$$\sigma_z = .052(20) \; \frac{10^4 + 0.3 - 20(1-1)}{1(20)}^1 \qquad (A-7)$$

$$\simeq 500$$

Figure A-2 plots all $\sigma_z$ for distances downwind to 100 km.

$\sigma_x$ = standard deviation of the downwind concentration distribution.

= 1 (using assumptions (1) and (12))

thus,

$$CCT/Q = \frac{1}{2\pi(500)(1)} = 3.14\times10^{-4} \text{ sec/m}^3 \qquad \text{(A-8)}$$

for a release altitude of 3 km at a distance of 10 km downwind.

VT = vertical term

$$= \exp\left[-1/2(\frac{H-z}{\sigma_z})^2\right] + \exp\left[-1/2(\frac{H+z}{\sigma_z})^2\right] +$$

$$\sum_{i=1}^{\infty} (\exp\left[-1/2(\frac{2iH_m-H-z}{\sigma_z})^2\right] + \exp\left[-1/2(\frac{2iH_m-H+z}{\sigma_z})^2\right]$$

$$+ \exp\left[-1/2(\frac{2iH_m+H-z}{\sigma_z})^2\right] + \exp\left[-1/2(\frac{2iH_m+H+z}{\sigma_z})^2\right] \qquad \text{(A-9)}$$

The vertical term refers to the expansion of the gas in the z-direction where for Run (1)

H = height of release = 3000 m

z = height of interest = 2 m (ground level)

$H_m$ = 3000 (see assumption (1))

$\sigma_z$ = 500 m (at 10 km)

for one iteration

$$VT = \exp\left[-1/2(\frac{3000-2}{500})^2\right] + \exp\left[-1/2(\frac{3000+2}{500})\right] +$$

$$\exp\left[-1/2(\frac{6000-3000-2}{500})^2\right] + \exp\left[-1/2(\frac{6000-3000+2}{500})^2\right]$$

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$$+ \exp\left[-1/2\left(\frac{6000+3000-2}{500}\right)^2\right] + \exp\left[-1/2\left(\frac{6000+3000+2}{500}\right)^2\right]$$

$$= \exp(-18) + \exp(-18) + \exp(-18) + \exp(-18)$$
$$+ \exp(-162) + \exp(-162) \tag{A-10}$$

$$VT = 4\exp(-18) + 2\exp(-162) \tag{A-11}$$

$$= 1.52 \times 10^{-8}$$

Only one iteration is used in the vertical term calculation because succeeding iterations become negligibly small relative to the total vertical term. Figure A-3 relates the vertical diffusion term with downwind distances.

$$EET = \int_{P_1}^{P_2} \frac{1}{\sqrt{2\pi}} \exp(-1/2p^2)\,dp$$

$$= \frac{-\exp(-1/2p^2)}{2\pi p} + \sum_{i=2}^{\infty} \left[\frac{-p^{-(2i-1)}}{\sum_{n=2}^{i}(2n-3)}\right]_{P_1}^{P_2} \qquad \text{(Turner (9:41))} \tag{A-12}$$

where

$$p_1 = \frac{y_1}{\sigma_y} \quad \text{and} \quad p_2 = \frac{y_2}{\sigma_y}$$

when the spray line stretches from $y_1$ to $y_2$,

and

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$$\sigma_y = \left[ \left( (\sigma_a'(\tau)) \, x_{ry} \left( \frac{x + x_y - x_{ry}(1-\alpha)}{\alpha x_{ry}} \right)^{\alpha} \right)^2 + \frac{(\Delta\theta' x)}{4.3} \right]^{1/2}$$

(A-13)

where

$$\sigma_a'(\tau) = (\sigma_a'(\tau_0)) \, (\frac{\tau}{\tau_0})^{1/5}$$

(A-14)

where

$\tau$ = emission time = 15 seconds

$\tau_0$ = reference time = 600 seconds

$\sigma_a'(\tau_0)$ = standard deviation of the angle measured over reference time ($\tau_0$)

$\simeq 15^0$ = .263 radians (from Cramer (3:53))

$\sigma_A'(\tau)$ = (.263) $(\frac{15}{600})^{1/5}$ = .263(.025)$^{.20}$

= 1.58x10$^{-4}$

$x_{ry}$ = distance at which crosswind cloud stabilization occurs downwind from source.

= 40 meters (from Dettling (4:12))

$x$ = 10$^4$ meters (from example in Equation A-7)

$x_y$ = crosswind virtual distance

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$$= \frac{\sigma_{ry}}{\sigma_A(\tau)} - x_{Ry} \qquad \text{(A-15)}$$

where

$\sigma_{yR}$ = standard deviation of the cross-wind distribution

$\quad$ = 1

$x_{Ry}$ = distance at which the standard deviation of crosswind concentration is measured

$\quad$ = 0

$\alpha$ = crosswind diffusion coefficient

$\quad$ = 1

$\Delta\theta$ = azimuth wind direction shear between ground level and release level

$$= \frac{\Delta\theta}{\Delta z} (z_2 - z_1) \qquad \text{(A-16)}$$

$\qquad$ where

$\quad \dfrac{\Delta\theta}{\Delta z}$ = rate change of wind direction from surface to release height (radians/meters)

Since the HF is released well above the gradient level, the angle between the surface and gradient level is assumed to be $45^\circ$ as estimated by Sutton (6:71).

$$= \frac{.14 \text{ radians}}{3000 \text{ meters}} \qquad \text{(A-17)}$$

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$$= 0.47 \times 10^{-4} \text{ radians/meters}$$

$z_2$ = effective upper bound of cloud

= 3000 meters

$z_1$ = effective lower bound of cloud

= 2 meters

$$\Delta\theta' = 0.47 \times 10^{-4}(3000-2) \qquad \text{(A-18)}$$
$$= .14$$

thus

$$\sigma_y = (1.58 \times 10^{-4}(40) \, (\frac{10^4 + 1 - 40(1-1)}{(1)40})^1)^2 + (\frac{.14 \times 10^4}{4.3})^2)^{1/2} \qquad \text{(A-19)}$$

= 811 meters (for a distance 10 km downwind)

Finally, to calculate the limits of the EET summation term

$y_{1,2}$ = distance from centerline of concentration

= 1725 meters

then

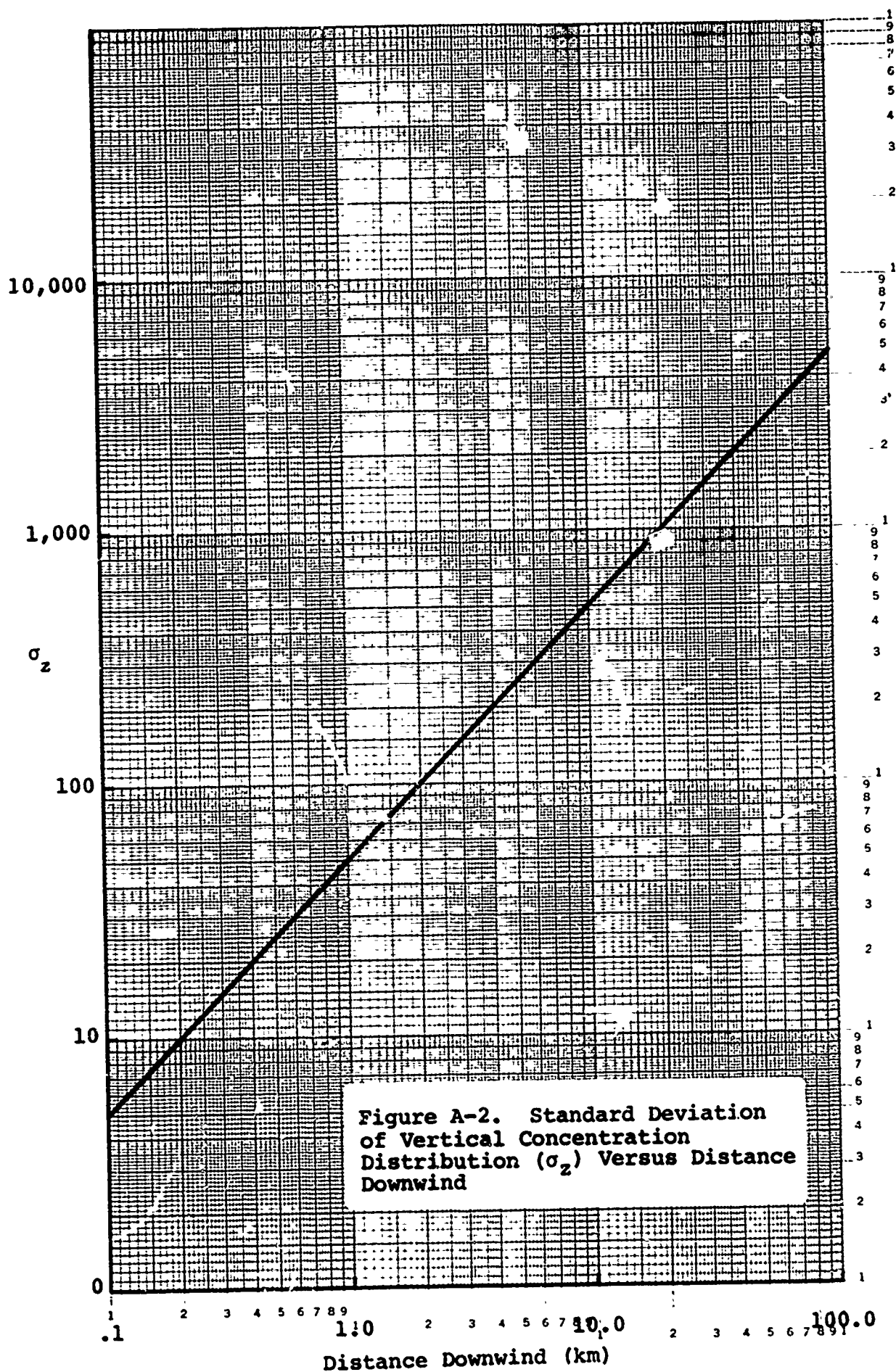$$P_{1,2} = \frac{y_{1,2}}{\sigma_y} = \frac{1725}{811} = 2.13 \qquad \text{(A-20)}$$

$$\text{EET} = \int_{-2.13}^{+2.13} \frac{1}{2\pi} \exp(-1/2(2.13)^2) \, dp \qquad \text{(A-21)}$$

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= .9668 (from Burrington (2:273)) for a sampling
   height of 2 m when HF is released from a height
   of 3 km.

Figure A-4 expresses EET relative to airplane speed at
release time.

AT = cloud growth in the along wind direction
   = 1 (using assumptions (1) and (13)

DT = depletion term or the loss of material by decay
   processes
   = 1 (using assumption (5))

Figure A-2. Standard Deviation of Vertical Concentration Distribution ($\sigma_z$) Versus Distance Downwind

Distance Downwind (km)
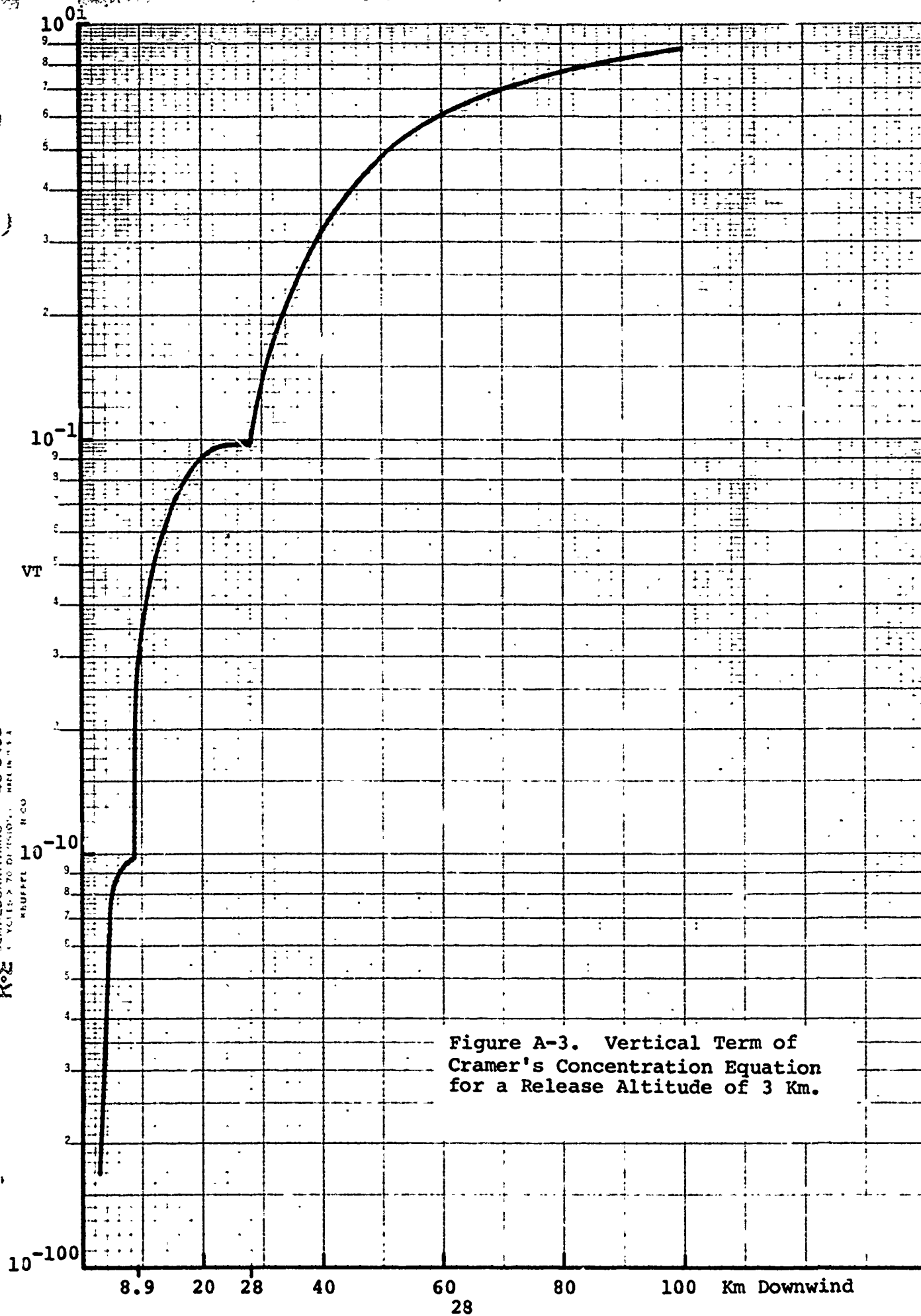
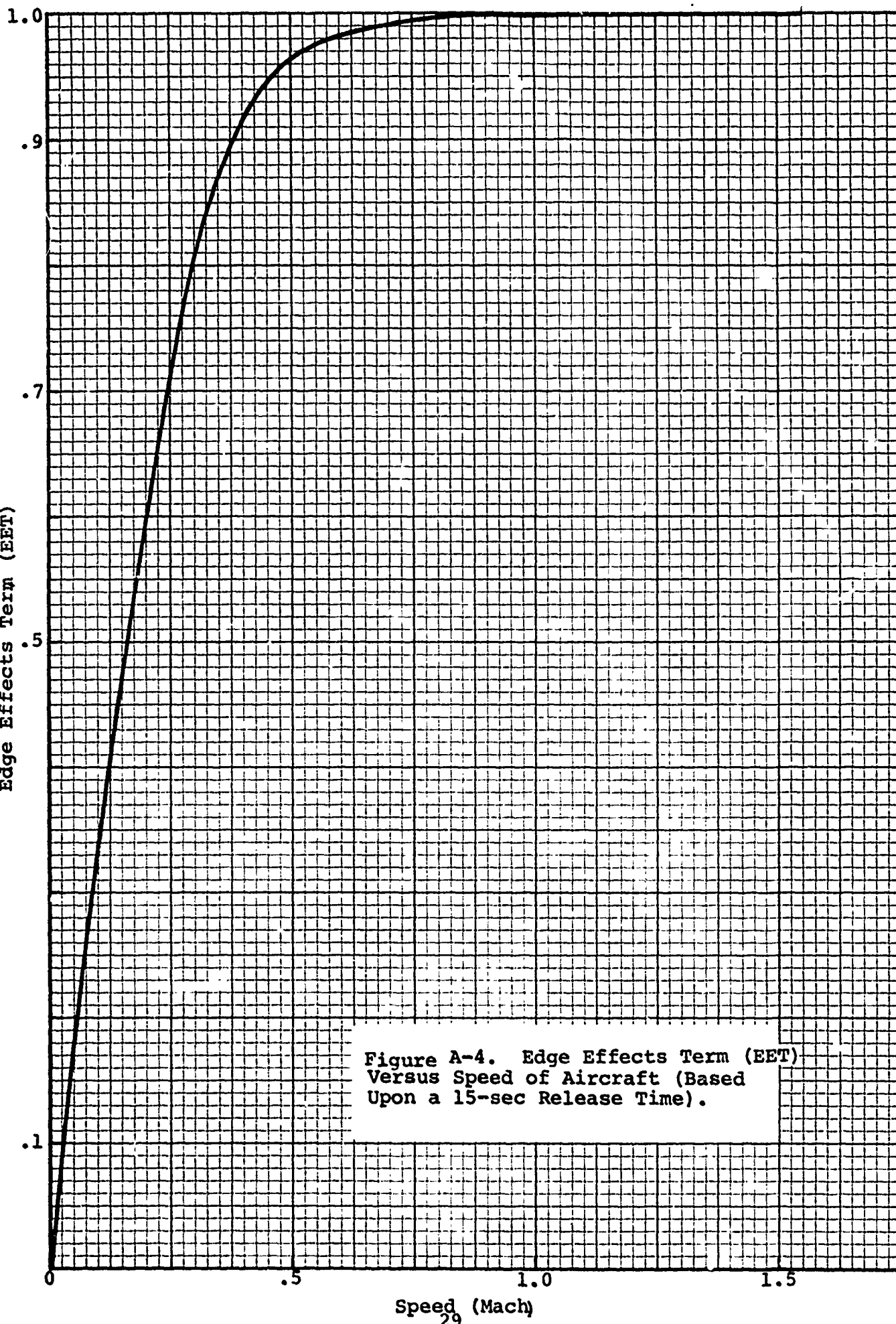Figure A-3. Vertical Term of Cramer's Concentration Equation for a Release Altitude of 3 Km.

Figure A-4. Edge Effects Term (EET)
Versus Speed of Aircraft (Based
Upon a 15-sec Release Time).

Edge Effects Term (EET)

Speed (Mach)